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Complexes of Thiourea with Alkali Metal Bromides and Iodides: Structural Properties, Mixed-Halide and Mixed-Metal Materials, and Halide Exchange Processes

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Abstract

We report the preparation and structural properties of complexes of metal halides and thiourea with composition $\text{MX}[\text{thiourea}]_4$ ($\text{MX} = \text{KBr}, \text{KI}, \text{RbI}, \text{CsI}$), together with the mixed-halide materials $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ ($0 < n < 1$) and the mixed-metal materials $\text{K}_n\text{Cs}_{1-n}\text{I}[\text{thiourea}]_4$ ($0 < n < 1$). These materials are isostructural, with a tetragonal structure (space group $P4/mnc$) characterized by $\text{M}^+[\text{thiourea}]_4$ coordination columns along the 4-fold axis and halide anions located in channels in the region of space between adjacent columns and running parallel to the columns. For the mixed-halide materials, the stoichiometry $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ depends on the bromide/iodide ratio in the crystallization solution; the crystalline complexes have a higher bromide/iodide ratio than the crystallization solution, indicating preferential incorporation of bromide within the complex. Soaking crystals of $\text{KBr}_{0.61}\text{I}_{0.39}[\text{thiourea}]_4$ in iodide containing solutions leads to halide exchange, with the iodide to bromide ratio increasing relative to the parent crystal. Further experiments produced no evidence that these thiourea complexes can accommodate extended polyiodide networks.

1. Introduction

Thiourea has long been used as a versatile complexing agent, and substantial progress has been made in understanding and exploiting the physicochemical properties of thiourea-ligated metal complexes.^{1–6} In addition, thiourea inclusion compounds containing branched hydrocarbons or cyclic molecules as the guest component within a thiourea host tunnel structure have received much attention for their interesting range of structural and physicochemical properties.^{7–16} However, much less attention has been devoted to structure-property relationships of complexes formed between thiourea and salts of monovalent cations which do not act as Lewis acids in the presence of chelating ligands (i.e. with no formation of covalent cation-sulfur bonds). Although a complex $\text{NH}_4\text{Br}[\text{thiourea}]_4$ was reported¹⁷ in 1888, it was only 80 years later that more detailed chemical and structural studies were reported by Boeyens and Herbstein.^{18,19} Their work confirmed that the NH_4Br component of this structure can be readily replaced by the chloride and iodide analogues or by certain alkali metal halides and thallium(I) salts, giving complexes with general formula $\text{MX}[\text{thiourea}]_4$.

In general, the $\text{MX}[\text{thiourea}]_4$ complexes crystallize as aggregates of delicate fibrous needles which are usually not suitable for single-crystal X-ray diffraction (XRD). For this reason, the crystal structures of most of these materials were not determined, and only their space group and unit cell parameters were derived from the combined examination of powder and single-crystal XRD data.¹⁹

The materials containing halide anions are of interest due to their potential to act as ionic conductors^{20,21} or as simple models for understanding charge-transport processes in biological ion channels.^{22,23} As discussed in this paper, the complexes formed between thiourea and alkali metal (K, Rb and Cs) bromides or iodides are isostructural, characterized by a tetragonal structure (space group $P4/mnc$). The fact that bromide and iodide form iso-structural complexes favours the prospects to design new mixed-halide complexes within this family – i.e. materials of composition $\text{MBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ ($0 < n < 1$). Within this perspective, the ability to control the bromide/iodide ratio is important, as small modifications of stoichiometry may give substantial changes in physicochemical properties.

Here we report the preparation and structural properties of complexes of thiourea with KBr, KI, RbI and CsI. Although the existence of these materials has been described previously, it is only in the case of $\text{RbI}[\text{thiourea}]_4$ that crystal structure determination has actually been reported.²⁴ Furthermore, we report new mixed-halide complexes within this family, with general formula $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ ($0 < n < 1$) and well-defined bromide to iodide ratios, and we explore the possibilities to carry out halide exchange processes for these materials. Finally, the formation and structural properties of mixed-metal materials of general formula $\text{K}_n\text{Cs}_{1-n}\text{I}[\text{thiourea}]_4$ ($0 < n < 1$) are also reported.

2. Experimental

2.1 Preparation of Materials

General Aspects

Thiourea (99%), potassium bromide (99%), potassium iodide (99%), rubidium iodide (99.9%), cesium iodide (99.9%), iodine (99.5%) and iodine monobromide (IBr, 98%) were obtained from Alfa Aesar and used without further purification. All complexes were prepared from methanol solution (HPLC grade), rather than the solvents (ethanol and/or water) reported previously.^{17,19,25} In the typical preparation procedure, the alkali metal halide (MX) was added to a solution of thiourea in methanol in a conical flask, which was immersed in a silicone oil bath at *ca.* 58 °C. At this stage, it was sometimes necessary to add a further small quantity of methanol to make the solution homogeneous. The solution was cooled to 20 °C in an incubator over *ca.* 32 hrs. If no crystallization occurred, the solution was transferred to a test tube covered with parafilm with pin-holes to allow slow evaporation of the solvent at ambient temperature.

Preparation of $MX[thiourea]_4$ Complexes ($MX = KBr, KI, RbI, CsI$)

The alkali metal halide (1.065 mmol) was added to a solution of thiourea (0.300 g, 3.941 mmol) in methanol (4 – 5 mL). For all complexes, slow evaporation produced aggregates of fibrous needles within 7 to 8 days. These aggregates were dried in air for a few hours and were highly crystalline. In the case of $KBr[thiourea]_4$, a few cubic crystals of pure KBr precipitated on the fourth day and were removed (powder XRD also showed a small amount of pure thiourea in the final product).

To explore the possibility of forming extended polyiodide networks²⁶ within this family of complexes, KI (0.124 g, 0.747 mmol) and I_2 (0.144 g, 0.567 mmol) were added simultaneously to a hot (*ca.* 58 °C) solution of thiourea (0.300 g, 3.941 mmol) in methanol (4 mL), which was then allowed to cool to 20 °C. The solution changed from reddish-brown to yellowish on cooling and a few golden-yellow crystals formed (shown by powder XRD to be pure sulfur). Slow solvent evaporation from the filtrate at ambient temperature produced fibrous needles within 7 to 8 days. The powder XRD pattern of this material was very similar to that of the $KI[thiourea]_4$ complex.

Preparation of $KBr_nI_{1-n}[thiourea]_4$ Complexes ($0 < n < 1$)

The first preparation of a mixed halide material involved addition of equi-molar quantities of KI (0.1090 g, 0.657 mmol) and KBr (0.0782 g, 0.657 mmol) to a solution containing thiourea (0.300 g, 3.941 mmol) in methanol (4 mL) at *ca.* 58 °C. The flask containing this solution was then immersed in a Dewar flask filled with hot water at the same temperature, and the crystallization assembly was

allowed to cool slowly to ambient temperature over *ca.* 20 hrs (the role of the Dewar flask was to provide thermal insulation to ensure slow cooling of the crystallization solution). Although no crystals were found to precipitate at this stage, subsequent slow solvent evaporation produced fibrous needles within 7 to 8 days. Additional experiments were carried with KI/KBr molar ratios of 2:1 [i.e. 0.145 g of KI (0.876 mmol) and 0.0521 g of KBr (0.438 mmol) were added to a solution of thiourea (0.300 g, 3.941 mmol) in methanol (4 mL)] and 3:1 [0.163 g of KI (0.984 mmol) and 0.0390 g of KBr (0.328 mmol) were added to a solution of thiourea (0.300 g, 3.941 mmol) in methanol (4 mL)]. In these experiments, solvent evaporation at ambient temperature yielded aggregates of fibrous needles after 7 to 8 days from both solutions. The powder XRD patterns of all three complexes were similar (and also indicated the presence of a small amount of pure thiourea).

A further modification involved simultaneous addition of KI (0.124 g, 0.747 mmol) and IBr (0.117 g, 0.566 mmol) to a hot solution of thiourea (0.300 g, 3.941 mmol) in methanol (4 mL). On cooling the solution, crystals of pure sulfur formed (as characterized by powder XRD) and were filtered off. Slow solvent evaporation of the resulting solution at ambient temperature produced fibrous needles after 8 days. The powder XRD pattern of this material was similar to those of the $\text{KBr}_n\text{I}_{(1-n)}[\text{thiourea}]_4$ complexes.

Preparation of $\text{Cs}_n\text{K}_{1-n}\text{I}[\text{thiourea}]_4$ Complexes ($0 < n < 1$)

Equi-molar quantities of KI (0.109 g, 0.657 mmol) and CsI (0.171 g, 0.657 mmol) were added to thiourea (0.300 g, 3.941 mmol) in hot methanol (4 mL). The solution was cooled in a Dewar flask, producing a large aggregate of fibrous needles, which also contained small amounts of pure KI and pure CsI.

Halide Exchange Processes

Halide exchange between pre-formed crystals of selected complexes and a solution phase containing a different halide composition was investigated as follows. Initially, a solution was prepared by adding I_2 (0.200 g, 0.788 mmol) and KI (0.172 g, 1.036 mmol) to methanol (20 mL) and heating to 40 °C under stirring, before filtering the solution and cooling to ambient temperature. Then, a few crystals of the $\text{KBr}[\text{thiourea}]_4$ complex (*ca.* 0.040 g) were placed in a test tube and covered by a small amount of the solution described above. The test tube was sealed and kept at ambient temperature for one week. The same procedure was carried out using crystals (*ca.* 0.015 g) of the mixed halide complex prepared from equi-molar quantities of KI and KBr.

2.2 Powder X-ray Diffraction

Powder XRD patterns were recorded on a Bruker D8 diffractometer (CuK α 1, Ge monochromated) operating in transmission mode. The sample was ground to a fine powder using a mortar and pestle, and placed between two pieces of Scotch tape, which was then inserted into a foil-type sample holder. The powder XRD data were recorded in the 2θ range 4° to 50° with step size 0.017° and a data collection time of 0.5 s per step.

2.3 Single-Crystal X-ray Diffraction

Single-crystal XRD data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator [using either CuK α ($\lambda = 1.5418 \text{ \AA}$) or MoK α ($\lambda = 0.7107 \text{ \AA}$) radiation], equipped with an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELX.^{27,28} In general, non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with U_{iso} set at 1.2 or 1.5 times the value of U_{eq} for the atom to which they are bonded. In the case of the mixed-halide materials KBr $_n$ I $_{1-n}$ [thiourea] $_4$, the bromide and iodide anions were located on the same sites; the relative occupancies of bromide and iodide on each site were refined, subject to the constraint that the total occupancy of the site was equal to one. In the case of the mixed-metal materials K $_n$ Cs $_{1-n}$ I[thiourea] $_4$, the potassium and cesium cations were located on the same sites; the relative occupancies of potassium and cesium on each site were refined, subject to the constraint that the total occupancy of the site was equal to one. Supplementary crystallographic data for the crystal structures reported in this paper are contained in CCDC 1515349 – 1515369 (the specific CCDC reference number for each crystal structure is indicated in Tables 1 – 6). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. In all cases, the crystal structure determined from single-crystal XRD data was consistent with the powder XRD pattern of the bulk polycrystalline sample from which the single crystal was selected.

3. Results and Discussion

3.1 MX[thiourea] $_4$ Materials

The complexes of metal halides and thiourea with composition MX[thiourea] $_4$ (MX = KBr, KI, RbI, CsI) are iso-structural, and are tetragonal with space group $P4/mnc$. Crystallographic data for all of these materials are given in Table 1. As a representative example, the crystal structure of the material KBr[thiourea] $_4$ is shown in Fig. 1. The crystal structure contains coordination columns of composition M $^+$ [thiourea] $_4$ running parallel to the c -axis. The halide anions are present in channels located in the region of space between groups of four adjacent columns, and also running parallel to the c -axis. The M $^+$ cations in a given column (Fig. 2a) are arranged linearly along the c -axis, and each M $^+$ cation is

coordinated by eight sulfur atoms (from thiourea molecules) at the corners of a cubically distorted Archimedean antiprism, with each S atom coordinating to two adjacent M^+ cations in the column. On moving along a coordination column (along the c -axis), M^+ cations alternate with groups of four thiourea molecules (Fig. 2a,b) for which the C=S bonds lie in the same plane (parallel to the ab -plane) and for which the sulfur atoms are coordinated to the same pair of M^+ cations. The orientations of the four thiourea molecules within one of these groups may be described as either “clockwise” (green molecules in Fig. 2b) or “anti-clockwise” (red molecules in Fig. 2b), with the clockwise and anti-clockwise groups alternating on moving along the c -axis. The halide (X^-) anions are linked to the coordination columns by weak $N-H\cdots X^-$ hydrogen-bonding interactions (see Fig. 2c), with each halide anion involved in eight interactions of this type to four thiourea molecules from four different columns (as the $H\cdots X^-$ distances in these interactions are close to the sum of van der Waals radii, we ascribe these interactions, at least on geometric grounds, as only weak hydrogen bonds). Finally, we note that the crystal structure contains two crystallographically distinct types of $M^+[thiourea]_4$ column (Fig. 3). In one type of column (denoted M1), the M^+ cations are located at $(0, \frac{1}{2}, \frac{1}{4})$ and symmetry related sites (multiplicity = 4; denoted K1 in the caption of Fig. 3). In the other type of column (denoted M2), the M^+ cations are located at $(0, 0, z)$ and symmetry related sites (multiplicity = 4; denoted K2 in the caption of Fig. 3). The two types of column have very similar geometric properties (Fig. 3a), and differ primarily in the precise orientation of the thiourea molecules coordinated to the M^+ cations (Fig. 3b). There are also slight differences in the distances between adjacent M^+ cations along the c -axis in the two types of column. In the columns denoted M1, all $M^+\cdots M^+$ distances are identical by symmetry (4.115 Å in the case of KBr[thiourea]₄), whereas in the columns denoted M2, the $M^+\cdots M^+$ distances alternate between two values (4.210 Å and 4.019 Å in the case of KBr[thiourea]₄).

The variation in unit cell parameters (particularly the unit cell volume) for the different $MX[thiourea]_4$ complexes studied are consistent with the change in the relative sizes of the halide anions and metal cations.¹⁹ Thus, the volume per formula unit increases by *ca.* 29.5 Å³ from KBr[thiourea]₄ to KI[thiourea]₄ (see Table 1).²⁹ With regard to variation of the metal cation, the unit cell volumes of the complexes increase in the order KI[thiourea]₄ < RbI[thiourea]₄ < CsI[thiourea]₄ in line with the increase in the ionic radius of the metal cation.

3.2 Mixed-Halide Materials $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$

To explore the possible formation of mixed halide complexes of general formula $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$, the crystallization procedure was carried out using mixtures of KI and KBr in different molar ratios. Crystallographic data for single crystals selected from the resultant samples of mixed halide materials are given in Tables 2 and 3. In each case, more than one single crystal was investigated in order to confirm the bromide/iodide ratio in the complexes. The mixed-halide materials $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ are iso-structural with the end-members $\text{KBr}[\text{thiourea}]_4$ and $\text{KI}[\text{thiourea}]_4$ containing a single type of halide anion. As shown in Fig. 4, there is an essentially linear relationship between the unit cell volume and the mole fraction of iodide (relative to total bromide plus iodide) in the mixed-halide materials $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$, in accordance with Vegard's Law.^{30,31}

For crystals prepared from an initial mole fraction of bromide (relative to total bromide plus iodide) in the crystallization solution of 0.5, the mole fractions of bromide in three single crystals examined were 0.61, 0.60 and 0.61 (Table 2). Similarly, from a solution with initial mole fraction of bromide of 0.33, the mole fractions of bromide in the two crystals studied were 0.52 and 0.50. And from a solution with initial mole fraction of bromide of 0.25, the mole fractions of bromide in the two crystals studied were 0.40 and 0.36 (Table 3). The fact that the mole fraction of bromide in the crystalline complexes is higher than the mole fraction of bromide in the crystallization solution indicates preferential uptake of bromide over iodide within the complexes. This observation may reflect an energetically more favourable situation for bromide over iodide in the crystalline complexes (in this regard, we note that bromide is generally considered to be a stronger hydrogen-bond acceptor than iodide³²) and/or may reflect an energetically less favourable situation for bromide over iodide in the crystallization solution (for example, lower solubility of bromide than iodide in the complex multi-component solution).

Not surprisingly, it is clear from our results that increasing the mole fraction of iodide in the crystallization solution leads to an increase in the mole fraction of iodide incorporated into the solid complexes $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ (but with the bromide to iodide ratio in the complex always higher than that in the crystallization solution, as noted above).

It follows from the above discussion that, in principle, the formation of mixed-halide complexes containing any desired bromide/iodide ratio may be achieved by appropriate choice of experimental conditions for the crystallization experiment. However, as discussed in more detail elsewhere,^{33,34} it is important to note that, in competitive crystallization processes of this type, the relative uptake of

the two competing species (in this case bromide and iodide anions) within the crystalline phase will generally change in a systematic manner as a function of progress of the crystallization process.

3.3 Mixed-Metal Materials $K_nCs_{1-n}I[\text{thiourea}]_4$

The formation of mixed-metal complexes $K_nCs_{1-n}I[\text{thiourea}]_4$ containing both K^+ and Cs^+ has also been achieved by crystallization from solutions containing both KI and CsI. Crystallographic and structure refinement data for two crystals grown from a solution prepared with equi-molar amounts of KI and CsI are shown in Table 4, with the mole fraction of K^+ (relative to total metal content) in the two crystals determined to be 0.40 and 0.03. The significantly different stoichiometries suggest that the preparative route may be ineffective for preparing materials with a reproducible stoichiometry (in contrast to the situation for the mixed-halide materials discussed above). However, we note that both the crystals studied have an excess of Cs^+ relative to K^+ , indicating preferential incorporation of Cs^+ over K^+ within the mixed-metal complexes.

3.4 Preparation of Materials in the Presence of I_2 or IBr

Thiourea complexes were also prepared from a solution containing KI and I_2 (in 4:3 molar ratio) and from a solution containing KI and IBr (in 4:3 molar ratio), and crystallographic data for the materials obtained are summarized in Table 5. The complex prepared from the KI/ I_2 solution was found to be $KI[\text{thiourea}]_4$, suggesting that incorporation of extended polyiodide networks²⁶ [for example $(I_3^-)_x$ or $(I_5^-)_x$] within this family of crystalline complexes does not occur.

The complex prepared from the KI/IBr solution was found to be a mixed-halide material containing both bromide and iodide anions, with significantly different mole fraction of bromide (0.24 and 0.09) in the two crystals studied (Table 5). The lack of reproducibility in the bromide/iodide ratio in these crystals may suggest that the bromide/iodide ratio in solution varies significantly with time. Chemical reactions with complex kinetic behaviour have been reported for thiourea in the presence of halogen containing oxidants,³⁵⁻³⁷ which may account for the small amount of pure sulfur precipitated in both crystallization solutions during cooling from 58 °C to 20 °C. According to Rábai and Beck,³⁵ the most likely source of elemental sulfur upon oxidation of thiourea by iodate in aqueous media (with thiourea in excess) is the hydrolytic disproportionation of dithiobisformamidine, which is produced in the first step of the parallel oxidation of thiourea by I_2 .

3.5 Halide Exchange Processes

The potential to carry out halide exchange processes within this family of complexes was explored by soaking crystals³⁸ of the $KBr[\text{thiourea}]_4$ and $KBr_{0.61}I_{0.39}[\text{thiourea}]_4$ complexes in small quantities

of a methanol solution containing KI and I₂ (in 4:3 molar ratio) at ambient temperature for a period of 7 days. Crystallographic and structure refinement data for crystals recovered following this procedure are given in Table 6. Two single crystals from each sample were studied to assess whether anion exchange occurs between the crystalline complexes and the solution phase (i.e. replacement of bromide by iodide in the crystal structures). For the crystals of KBr[thiourea]₄, the resultant crystals were identical to the original crystals, with no evidence for incorporation of iodide. However, in the case of the crystals of KBr_{0.61}I_{0.39}[thiourea]₄, the composition was found to change during the soaking experiment, with the two crystals studied having mole fractions of iodide (relative to total bromide plus iodide) of 0.57 and 0.59, consistent with the uptake of iodide from the solution by the crystals with a corresponding loss of bromide from the crystals.

The different behaviour of KBr[thiourea]₄ and KBr_{0.61}I_{0.39}[thiourea]₄ in these experiments is surprising given that both complexes have the same types of channel that are expected to allow diffusion of iodide anions from the solution into the crystal with displacement of bromide anions. The fact that the halide anion exchange process was observed only for KBr_{0.61}I_{0.39}[thiourea]₄ (at least under the conditions of our experiments) suggests that the presence of iodide anions already in the complex may facilitate the halide exchange process.

As already described, soaking of crystals of the mixed-halide material KBr_{0.61}I_{0.39}[thiourea]₄ for a period of 7 days led to a moderate increase in the mole fraction of iodide in the complex from 0.39 to *ca.* 0.58 (Table 6). Increasing the soaking period to 11 days led to a larger increase in the mole fraction of iodide in the complex from 0.39 to 0.70 (Table 6). The main factors contributing to this behaviour include the relative sizes of the bromide and iodide anions and the initial bromide/iodide ratio in the crystallization solution. We note that, in spite of the relatively long soaking times, there was no evidence that the crystals studied had undergone any significant loss of crystalline integrity.³⁸

4. Concluding Remarks

Four complexes of thiourea with general composition MX[thiourea]₄ (MX = KBr, KI, RbI, CsI) have been prepared and their crystal structures have been determined from single-crystal XRD data. The materials studied have essentially the same tetragonal structure (space group *P4/mnc*), constructed from infinite M⁺[thiourea]₄ coordination columns that run parallel to the *c*-axis, with the X[−] anions located in channels between these columns.

Mixed-halide complexes with composition KBr_{*n*}I_{1−*n*}[thiourea]₄ (0 < *n* < 1) have also been prepared for the first time, and are iso-structural to the end-members with *n* = 0 and *n* = 1. The bromide/iodide ratio in the crystals depends on the initial bromide/iodide ratio in the crystallization solution, with

incorporation of bromide favoured relative to iodide. Similarly, mixed-metal complexes with composition $K_nCs_{1-n}I[\text{thiourea}]_4$ have been prepared by crystallization from solutions containing thiourea, KI and CsI, with preferential incorporation of Cs^+ over K^+ within the complex. Clearly, an interesting area for further investigation would be to apply techniques of computational chemistry to gain a deeper understanding of the preferential incorporation of Br^- over I^- in the mixed-halide materials and the preferential incorporation of Cs^+ over K^+ in the mixed-metal materials.

Finally, soaking crystals of the complex $KBr_{0.61}I_{0.39}[\text{thiourea}]_4$ in small quantities of a methanol solution containing iodide anions at ambient temperature led to a change in the bromide/iodide ratio in the complex, corresponding to an increase in the iodide content and suggesting that halide exchange occurs between the crystal and the solution phases. The presence of iodide anions in the original crystals appears to be crucial for facilitating the diffusion of iodide anions from the solution into the crystal (and the consequent loss of bromide from the crystal), as no halide exchange was observed in the corresponding experiment carried out for crystals of the complex $KBr[\text{thiourea}]_4$.

In summary, the insights reported here on the structural properties, crystal growth and halide exchange processes of complexes of thiourea with alkali metal halides are of fundamental importance, while the potential for developing applications of these materials (such as ionic conductivity and dielectric properties) remains to be explored. Research studies along these lines are currently in progress.

ASSOCIATED CONTENT

Supporting Information

Supplementary crystallographic data for the crystal structures reported in this paper are contained in CCDC 1515349 – 1515369 (the specific CCDC reference number for each crystal structure is indicated in Tables 1 – 6). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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Notes

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Table 1 Crystal data and structure refinement results for complexes with composition MX[thiourea]₄ (MX = KBr, KI, RbI, CsI).

Material	KBr[thiourea] ₄	KI[thiourea] ₄	RbI[thiourea] ₄	CsI[thiourea] ₄
CCDC Reference	1515367	1515365	1515368	1515352
Formula	KBr(SCN ₂ H ₄) ₄	KI(SCN ₂ H ₄) ₄	RbI(SCN ₂ H ₄) ₄	CsI(SCN ₂ H ₄) ₄
Molar mass (g mol ⁻¹)	423.50	470.49	516.86	564.30
Temperature (K)	296(2)	293(2)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71073	1.54184	0.71073
Crystal system, space group	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>
Unit cell parameters	$a = b = 19.7105(12) \text{ Å}$ $c = 8.2292(7) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.345(2) \text{ Å}$ $c = 8.2943(16) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.3139(3) \text{ Å}$ $c = 8.3464(2) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.5279(6) \text{ Å}$ $c = 8.4557(5) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$
Volume (Å ³)	3197.1(5)	3433.3(9)	3444.18(13)	3563.2(3)
Z	8	8	8	8
Density (g/cm ³)	1.760	1.820	1.994	2.104
Crystal size (mm ³)	0.373 × 0.031 × 0.023	0.359 × 0.049 × 0.043	0.497 × 0.028 × 0.021	0.321 × 0.060 × 0.029
Goodness-of-fit	1.054	1.062	1.026	1.049
Final <i>R</i> -factors <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0539 / 0.1131	0.0314 / 0.0678	0.0299 / 0.0766	0.0275 / 0.0534

Table 2 Crystal data and structure refinement results for three crystals of the thiourea complex prepared in a methanol solution with initial KI/KBr molar ratio of 1:1.

Material	KBr _{0.61} I _{0.39} [thiourea] ₄	KBr _{0.60} I _{0.40} [thiourea] ₄	KBr _{0.61} I _{0.39} [thiourea] ₄
CCDC Reference	1515349	1515366	1515354
Formula	KBr _{0.61} I _{0.39} (SCN ₂ H ₄) ₄	KBr _{0.60} I _{0.40} (SCN ₂ H ₄) ₄	KBr _{0.61} I _{0.39} (SCN ₂ H ₄) ₄
Molar mass (g mol ⁻¹)	442.06	442.29	442.00
Temperature (K)	293(2)	293(2)	296(2)
Wavelength (Å)	1.54184	0.71073	0.71073
Crystal system, space group	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>
Unit cell parameters	$a = b = 20.0373(4) \text{ Å}$ $c = 8.2801(3) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.0197(13) \text{ Å}$ $c = 8.2903(9) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.0041(14) \text{ Å}$ $c = 8.2598(11) \text{ Å}$ $\alpha = \beta = \gamma = 90^\circ$
Volume (Å ³)	3324.41(18)	3322.7(6)	3305.3(6)
Z	8	8	8
Density (g/cm ³)	1.766	1.768	1.776
Occupancy of Br ⁻	0.605(4)	0.600(6)	0.606(8)
Crystal size (mm ³)	0.192 × 0.020 × 0.013	0.191 × 0.147 × 0.033	0.350 × 0.021 × 0.020
Goodness-of-fit	1.039	1.070	1.029
Final <i>R</i> -factors <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0250 / 0.0554	0.0359 / 0.0587	0.0407 / 0.0638

Table 3 Crystal data and structure refinement results for: (i) two crystals of the thiourea complex prepared in a methanol solution with initial KI/KBr molar ratio of 2:1, and (ii) two crystals of the thiourea complex prepared in a methanol solution with initial KI/KBr molar ratio of 3:1.

Material	Preparation with KI/KBr Molar Ratio of 2:1		Preparation with KI/KBr Molar Ratio of 3:1	
	KBr _{0.52} I _{0.48} [thiourea] ₄	KBr _{0.50} I _{0.50} [thiourea] ₄	KBr _{0.40} I _{0.60} [thiourea] ₄	KBr _{0.36} I _{0.64} [thiourea] ₄
CCDC Reference	1515351	1515350	1515358	1515356
Formula	KBr _{0.52} I _{0.48} (SCN ₂ H ₄) ₄	KBr _{0.50} I _{0.50} (SCN ₂ H ₄) ₄	KBr _{0.40} I _{0.60} (SCN ₂ H ₄) ₄	KBr _{0.36} I _{0.64} (SCN ₂ H ₄) ₄
Molar mass (g mol ⁻¹)	446.29	447.05	451.93	453.34
Temperature (K)	150(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	1.54184	0.71073	0.71073
Crystal system, space group	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>
Unit cell parameters	$a = b = 19.9250(10)$ Å $c = 8.2205(6)$ Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.0603(3)$ Å $c = 8.2741(2)$ Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.0944(9)$ Å $c = 8.2605(5)$ Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.1441(11)$ Å $c = 8.2727(5)$ Å $\alpha = \beta = \gamma = 90^\circ$
Volume (Å ³)	3263.6(4)	3329.63(13)	3335.5(4)	3356.9(4)
Z	8	8	8	8
Density (g/cm ³)	1.817	1.784	1.800	1.794
Occupancy of Br ⁻	0.516(8)	0.498(8)	0.396(6)	0.362(7)
Crystal size (mm ³)	0.230 × 0.016 × 0.016	0.356 × 0.032 × 0.023	0.294 × 0.028 × 0.023	0.274 × 0.021 × 0.013
Goodness-of-fit	1.005	1.047	1.064	0.997
Final <i>R</i> -factors <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0433 / 0.0655	0.0416 / 0.1104	0.0421 / 0.0642	0.0536 / 0.0597

Table 4 Crystal data and structure refinement results for two crystals of the thiourea complex prepared in a methanol solution with initial KI/CsI molar ratio of 1:1.

Material	$\text{K}_{0.40}\text{Cs}_{0.60}\text{I}[\text{thiourea}]_4$	$\text{K}_{0.03}\text{Cs}_{0.97}\text{I}[\text{thiourea}]_4$
CCDC Reference	1515359	1515364
Formula	$\text{K}_{0.40}\text{Cs}_{0.60}\text{I}(\text{SCN}_2\text{H}_4)_4$	$\text{K}_{0.03}\text{Cs}_{0.97}\text{I}(\text{SCN}_2\text{H}_4)_4$
Molar mass (g mol^{-1})	527.12	561.25
Temperature (K)	297(2)	293(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system, space group	Tetragonal, $P4/mnc$	Tetragonal, $P4/mnc$
Unit cell parameters	$a = b = 20.3971(5) \text{ \AA}$ $c = 8.3656(3) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.4836(6) \text{ \AA}$ $c = 8.4275(4) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume (\AA^3)	3480.4(2)	3536.0(3)
Z	8	8
Density (g/cm^3)	2.012	2.109
Occupancies of the two independent K^+ sites	0.460(3), 0.330(3)	0.019(3), 0.040(3)
Crystal size (mm^3)	$0.337 \times 0.051 \times 0.045$	$0.262 \times 0.026 \times 0.022$
Goodness-of-fit	1.119	1.054
Final R -factors $R1/wR2$ [$I > 2\sigma(I)$]	0.0268 / 0.0506	0.0320 / 0.0466

Table 5 Crystal data and structure refinement results for: (i) a crystal of the thiourea complex prepared in a methanol solution containing KI and I₂, and (ii) two crystals of the thiourea complex prepared in a methanol solution containing KI and IBr.

Material	Thiourea + KI + I ₂	Thiourea + KI + IBr	
	KI[thiourea] ₄	KBr _{0.24} I _{0.76} [thiourea] ₄	KBr _{0.09} I _{0.91} [thiourea] ₄
CCDC Reference	1515355	1515353	1515369
Formula	KI(SCN ₂ H ₄) ₄	KBr _{0.24} I _{0.76} (SCN ₂ H ₄) ₄	KBr _{0.09} I _{0.91} (SCN ₂ H ₄) ₄
Molar mass (g mol ⁻¹)	470.48	459.27	466.26
Temperature (K)	293(2)	296(2)	293(2)
Wavelength (Å)	1.54184	1.54184	0.71073
Crystal system, space group	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>	Tetragonal, <i>P4/mnc</i>
Unit cell parameters	$a = b = 20.2952(2)$ Å $c = 8.26150(10)$ Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.1825(5)$ Å $c = 8.2676(4)$ Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.2697(9)$ Å $c = 8.2715(5)$ Å $\alpha = \beta = \gamma = 90^\circ$
Volume (Å ³)	3402.87(8)	3367.7(2)	3398.4(4)
Z	8	8	8
Density (g/cm ³)	1.837	1.812	1.823
Occupancy of Br ⁻	–	0.239(7)	0.090(7)
Crystal size (mm ³)	0.267 × 0.217 × 0.175	0.254 × 0.057 × 0.041	0.278 × 0.019 × 0.013
Goodness-of-fit	1.069	1.070	1.037
Final <i>R</i> -factors <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0261 / 0.0663	0.0332 / 0.0857	0.0483 / 0.0561

Table 6 Crystal data and structure refinement results for: (i) two crystals obtained after soaking crystals of $\text{KBr}[\text{thiourea}]_4$ in a methanol solution containing KI and I_2 for 7 days, (ii) two crystals obtained after soaking crystals of $\text{KBr}_{0.61}\text{I}_{0.39}[\text{thiourea}]_4$ in a methanol solution containing KI and I_2 for 7 days, (iii) a crystal obtained after soaking crystals of $\text{KBr}_{0.61}\text{I}_{0.39}[\text{thiourea}]_4$ in a methanol solution containing KI and I_2 for 11 days.

Material	Crystals obtained after soaking crystals of $\text{KBr}[\text{thiourea}]_4$ in a solution containing KI and I_2 for 7 days		Crystals obtained after soaking crystals of $\text{KBr}_{0.61}\text{I}_{0.39}[\text{thiourea}]_4$ in a solution containing KI and I_2 for 7 days	
	$\text{KBr}[\text{thiourea}]_4$	$\text{KBr}[\text{thiourea}]_4$	$\text{KBr}_{0.43}\text{I}_{0.57}[\text{thiourea}]_4$	$\text{KBr}_{0.41}\text{I}_{0.59}[\text{thiourea}]_4$
CCDC Reference	1515357	1515363	1515362	1515361
Formula	$\text{KBr}(\text{SCN}_2\text{H}_4)_4$	$\text{KBr}(\text{SCN}_2\text{H}_4)_4$	$\text{KBr}_{0.43}\text{I}_{0.57}(\text{SCN}_2\text{H}_4)_4$	$\text{KBr}_{0.41}\text{I}_{0.59}(\text{SCN}_2\text{H}_4)_4$
Molar mass (g mol^{-1})	423.50	423.50	450.16	452.87
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (\AA)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, $P4/mnc$	Tetragonal, $P4/mnc$	Tetragonal, $P4/mnc$	Tetragonal, $P4/mnc$
Unit cell parameters	$a = b = 19.8518(15) \text{ \AA}$ $c = 8.2760(10) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 19.7923(13) \text{ \AA}$ $c = 8.2439(10) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.181(3) \text{ \AA}$ $c = 8.292(2) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = 20.1367(19) \text{ \AA}$ $c = 8.2920(11) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume (\AA^3)	3261.5(6)	3229.4(6)	3377.3(13)	3362.3(8)
Z	8	8	8	8
Density (g/cm^3)	1.725	1.742	1.771	1.789
Occupancy of Br^-	0.998(3)	1.006(3)	0.43(2)	0.410(11)
Crystal size (mm^3)	$0.350 \times 0.033 \times 0.023$	$0.321 \times 0.026 \times 0.024$	$0.190 \times 0.020 \times 0.013$	$0.221 \times 0.026 \times 0.018$
Goodness-of-fit	0.982	1.041	0.958	0.982
Final R -factors $R1/wR2$ [$I > 2\sigma(I)$]	0.0473 / 0.0601	0.0497 / 0.0811	0.0550 / 0.0864	0.0481 / 0.0804

Material	Crystal obtained after soaking crystals of $\text{KBr}_{0.61}\text{I}_{0.39}[\text{thiourea}]_4$ in a solution containing KI and I_2 for 11 days
	$\text{KBr}_{0.30}\text{I}_{0.70}[\text{thiourea}]_4$
CCDC Reference	1515360
Formula	$\text{KBr}_{0.30}\text{I}_{0.70}(\text{SCN}_2\text{H}_4)_4$
Molar mass (g mol^{-1})	456.33
Temperature (K)	296(2)
Wavelength (\AA)	0.71073
Crystal system, space group	Tetragonal, $P4/mnc$
Unit cell parameters	$a = b = 20.2000(16) \text{ \AA}$, $c = 8.2882(8) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume (\AA^3)	3381.9(6)
Z	8
Density (g/cm^3)	1.792
Occupancy of Br^-	0.299(11)
Crystal size (mm^3)	$0.302 \times 0.022 \times 0.019$
Goodness-of-fit	1.006
Final R -factors $R1/wR2$ [$I > 2\sigma(I)$]	0.0464/0.0801

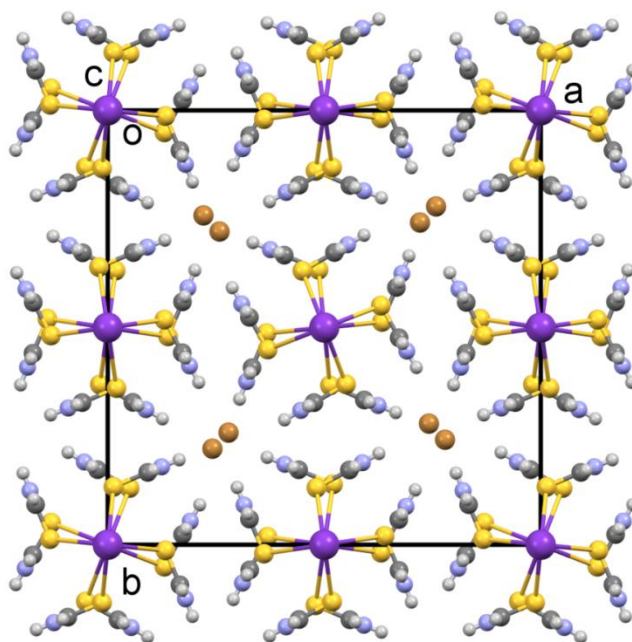


Figure 1 Crystal structure of the $\text{KBr}[\text{thiourea}]_4$ complex viewed along the c -axis, parallel to the infinite $\text{K}^+[\text{thiourea}]_4$ coordination columns which are held together by $\text{K}^+\cdots\text{S}=\text{C}(\text{NH}_2)_2$ interactions (brown, Br^- ; yellow, S; blue, N; grey, C; white, H; purple, K^+). The Br^- anions are located in channels between adjacent coordination columns; the channels also run along the c -axis.

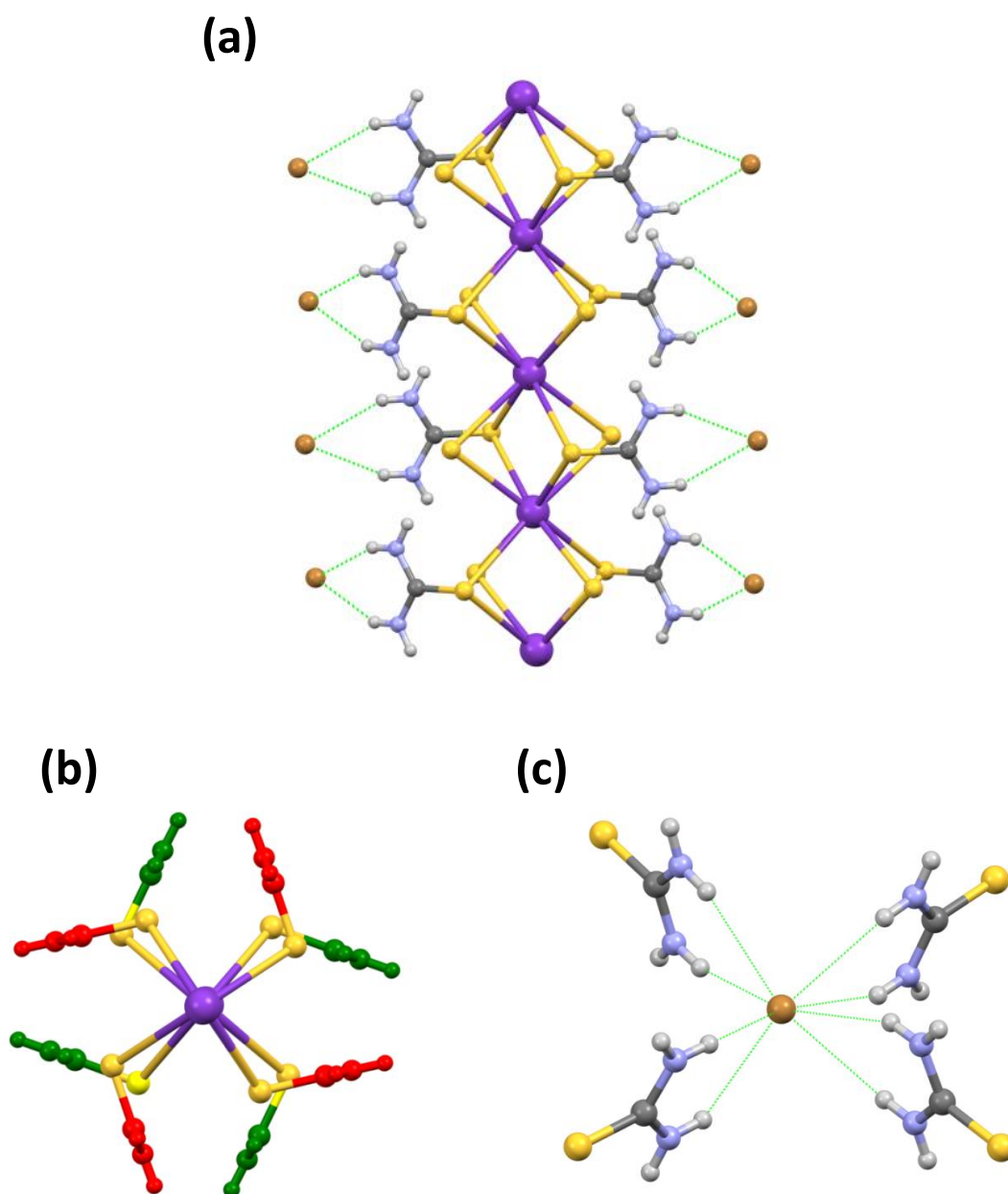


Figure 2 (a) A single K⁺[thiourea]₄ coordination column in the crystal structure of KBr[thiourea]₄, viewed perpendicular to the *c*-axis, which is vertical (the non-sulfur atoms of some thiourea molecules are omitted for clarity). Each thiourea molecule is involved in two C=S⋯K⁺ interactions, with C=S⋯K⁺ angles in the range 96.9(2)° to 105.9(2)°. Green dashed lines indicate N–H⋯Br[−] hydrogen bonds between thiourea molecules and Br[−] anions. (b) A single K⁺[thiourea]₄ coordination column viewed along the *c*-axis. The thiourea molecules are arranged in groups of four molecules, with the C=S bonds of all four molecules lying in the same plane (parallel to the *ab*-plane). The orientation of the four thiourea molecules within one of these groups is either clockwise (green molecules) or anti-clockwise (red molecules); clockwise and anti-clockwise groups alternate on moving along the *c*-axis. (c) The local structure around each Br[−] anion, comprising eight N–H⋯Br[−] hydrogen-bonding interactions involving four different thiourea molecules as the donors (N⋯Br[−] distances, 3.55 Å to 3.68 Å; N–H⋯Br[−] angles, 153° to 159°).

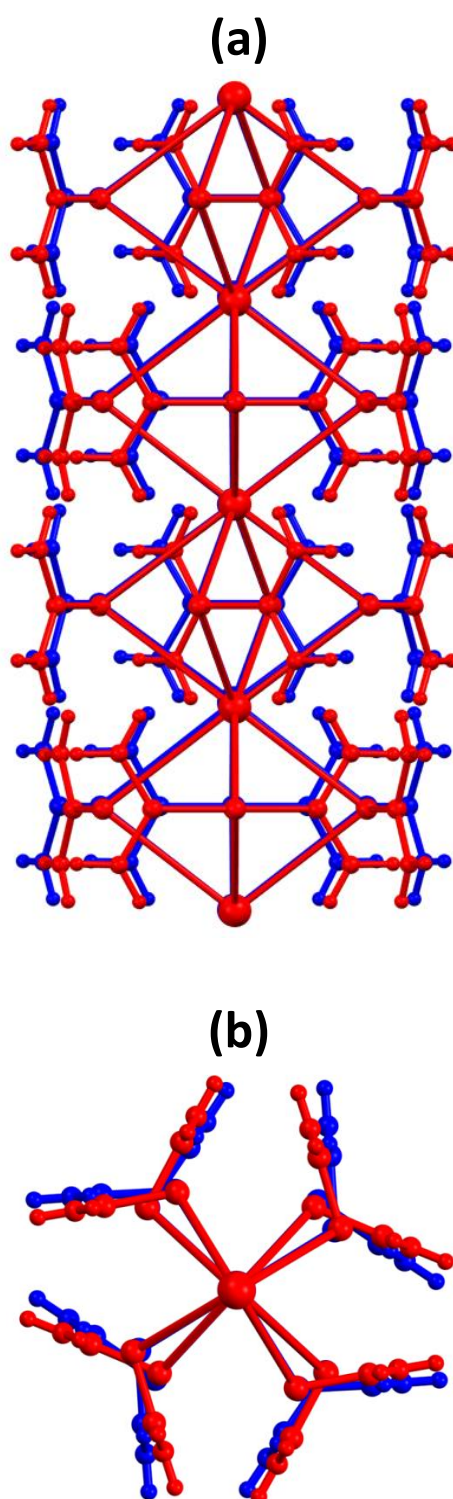


Figure 3 Overlays of the two types of $\text{K}^+[\text{thiourea}]_4$ coordination column in the crystal structure of $\text{KBr}[\text{thiourea}]_4$ viewed: (a) perpendicular to the c -axis, and (b) parallel to the c -axis. The column defined in the text as M1 (containing the K1 site in $\text{KBr}[\text{thiourea}]_4$) is shown in red. The column defined in the text as M2 (containing the K2 site in $\text{KBr}[\text{thiourea}]_4$) is shown in blue.

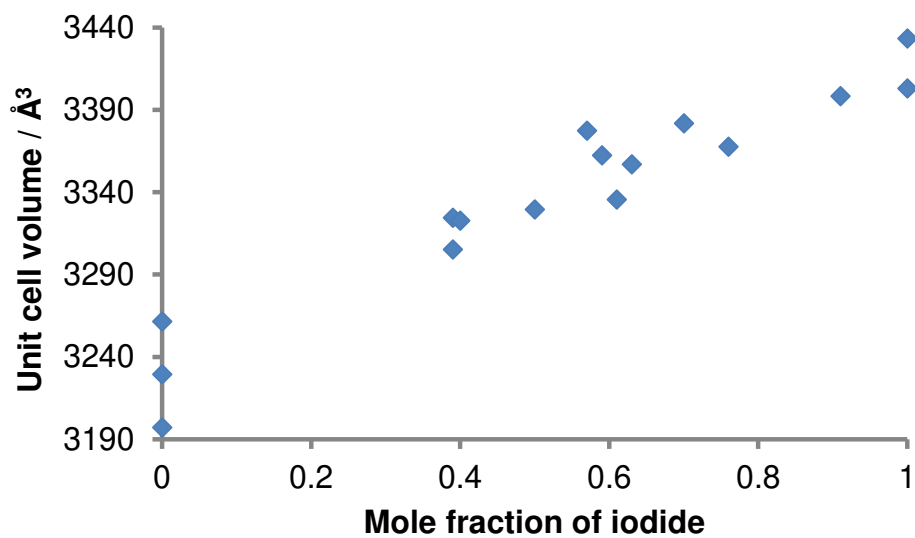
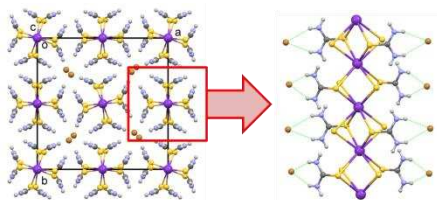


Figure 4 Unit cell volume *versus* mole fraction of iodide (relative to total bromide plus iodide) for the $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ structures determined at ambient temperature.

For Table of Contents Use Only

Complexes of Thiourea with Alkali Metal Bromides and Iodides: Structural Properties, Mixed-Halide and Mixed-Metal Materials, and Halide Exchange Processes

Vasileios G. Charalampopoulos, Benson M. Kariuki and Kenneth D.M. Harris*



Structural properties of a family of complexes of metal halides and thiourea with composition $\text{MX}[\text{thiourea}]_4$ ($\text{MX} = \text{KBr}, \text{KI}, \text{RbI}, \text{CsI}$) are reported, together with mixed-halide materials $\text{KBr}_n\text{I}_{1-n}[\text{thiourea}]_4$ and mixed-metal materials $\text{K}_n\text{Cs}_{1-n}\text{I}[\text{thiourea}]_4$. Halide exchange processes between crystals of these complexes and halide-containing solution phases are also explored.